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High-performance organosilicon compounds for energy storage

New Advanced Stable Electrolytes for High Voltage Electrochemical Energy Storage

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Project ID: ES271

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DOE Annual Merit Review Meeting June 8th, 2017

Overview

Timeline

- Project start date: 10/01/2015
- Project end date: 09/30/2017
- Percent complete: 90%

Budget

- Total project funding: $ 1,665 K
  - DOE (Silatronix): $897 K
  - Contractor share: $333 K
  - DOE (Subcontractor): $435K
- DOE (Silatronix) for FY16: $470 K
- DOE (Silatronix) for FY17: $427 K

Barriers

- Electrolyte development for
  - High voltage stability
  - Good thermal stability
  - Stable SEI layer to improve cycle life

Partners

- US Army Research Laboratory
- Argonne National Laboratory

Objective and Relevance

Project Objective: Develop an electrolyte system stable at high voltage (≥ 5V) to enable the development of high energy density Li-ion batteries required by the automotive industry.

Relevance: This technology, if successful, will have a significant impact on the enablement of high voltage cathode materials in Li-ion battery technology. In turn, this will provide a significant pathway for the development of higher energy density electrochemical storage devices, which is critical to expanding the electrification of the US vehicle fleet.

Specific Technical Metrics:

- Oxidative Stability
  - Breakdown voltage > 6 V (vs. Li/Li^+)
  - Parasitic current < 0.02 mA/cm^2 (at 6 V and 50°C)
- High Voltage System Performance
  - Initial capacity ≥ carbonate control (e.g. 5V LNMO system)
  - > 80% initial capacity remaining after 300 cycles at ≥ 55°C

Project Milestones

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Milestones for FY2016:

Milestones and Go/No-Go Decision	Milestone Verification Process	Date	Status
Baseline characterization: Oxidative breakdown of control electrolytes	Linear scan voltammetry and cyclic voltammetry at Silatronix	Nov. 2015	Complete
Characterize synthesized LCP	Verify structure and purity of LCP at ARL	Jan. 2016	Complete
Characterization of 2-3 new HV OS solvents/additives	Purity (>98%) and H_2O (<20ppm) at Silatronix	Apr. 2016	Complete
Go/No-Go Decision: Feasibility of HV performance demonstrated in ref. cells through determination of oxidative breakdown	Linear scan voltammetry (> 6V); Parasitic current 4.5-6.5V at 50°C (<0.02 mAh/cm^2 at 6V) at Silatronix	Jun. 2016	Complete
New HV OS solvents /additives synthesized	NMR verification of structures (4-6) at Silatronix	Aug. 2016	Complete
New HV co-solvents /additives synthesized	4-6 compounds prepared at ARL	Sep. 2016	Complete
Electrochemical evaluation, analysis, and diagnosis of new materials	CV, EIS, leakage current in half-cells at Silatronix	Sep. 2016	Complete

Project Milestones

Milestones for FY2017:

Milestones and Go/No-Go Decision	Milestone Verification Process	Date	Status
Compatibility screening with cathode half cells (LMNO/Li)	30°C cycling and parasitic current (4.5-5.3V) at Silatronix	Nov. 2016	Complete
Manufacture multilayer pouch cells for large pouch cell builds	32 LMNO/graphite multilayer pouch cells manufactured at ANL	Dec. 2016	Complete
Performance Testing of Final Pouch Cell Build: Cycle stability at 30°C and 55°C, Pouch swelling at 30°C complete	4 top formulations; cycle stability (capacity loss %, mAh/g), pouch swelling (thickness %, mm) at ANL	Jun. 2017	In Progress
Observed results extrapolated to DOE roadmap	Analysis of data, extrapolate to Roadmap electrodes at Silatronix	Jun. 2017	In Progress

Approach and Strategy

- Silatronix and ARL are synthesizing new materials based upon rational molecular design to achieve the superior oxidative stability required for HV applications.
- The fundamental electrochemical behavior of these materials is studied in reference cells to determine the oxidative breakdown voltage and mechanism of breakdown to produce a library of materials with superior fundamental oxidative stability for evaluation.
- The performance and safety of the new HV solvents and additives in formulated electrolytes are evaluated with the HV cathodes (5V LNMO) provided by ANL.
- Limited surface analysis is conducted after cycling to identify underlying mechanisms of degradation (i.e., surface film formation, metal dissolution, cathode morphology changes).
- Differential scanning calorimetry (DSC) is conducted on de-lithiated cathode material to understand the safety impact of the new HV materials.
- Solvation studies, using ESI-MS and NMR spectroscopy methods, are conducted to understand the Li^+ solvation behavior of the new OS solvents.
- Top performing HV formulations are tested in 5V LNMO pouch cells (13 layers, 200-300 mAh) at ANL. The pouch cell analysis focuses on cycling stability and pouch swelling.

Technical Accomplishment: Fundamental Mechanistic Studies of New Electrolyte Materials

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- OS solvents shows excellent oxidative stability in Pt reference system with a wider electrochemical stability window and lower parasitic currents above 4.5V compared to the EC/EMC (3/7, %v) carbonate control.
  - 12 OS solvents have been synthesized and evaluated.
  - 4 OS solvents met the Go/No Go technical metric (see Objectives).

- Additive selection is an important factor in full cell cycling performance, especially for OS electrolytes. Army Research Laboratory synthesized and screened ten additives for performance improvement. Five additives were shipped to Silatronix for evaluation.

Technical Accomplishment : Preliminary Screening of OS Solvents

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OS Solvents vs Control: Physical Properties

OS	Neat Solvent Properties			Electrolyte Properties (w/1M $LiPF_6$) at 30 °C No co-solvent	
	Dielectric	Flash	Density	Conductivity	Viscosity
EC/EMC (3/7)	22.1	<30	1.10	10	3.1
OS3	16.8	82	0.93	2.8	8.0
OS3a	18.2	78	1.09	3.5	7.9
OS3b	15.7	94	0.91	1.9	10.3
OS3c	17.9	98	1.03	2.3	11.5
OS3d	TBD	180	1.1	TBD	
OS4a	7.3	68	0.97	1.53	6.09
OS4b	6.6	76	1.11	0.43	7.92

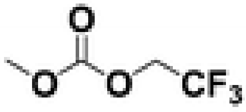
All OS solvents provide significantly higher flash points than carbonate control, with good conductivity and viscosity in electrolyte blends.

Select OS3 Family Solvents (Similar functional group to OS3, with great voltage stability)

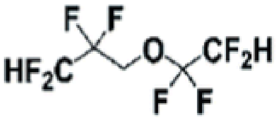
Solid at 30°C

OS Solvents with different functional group than OS3

Technical Accomplishment : LSV of OS3 Family Solvents

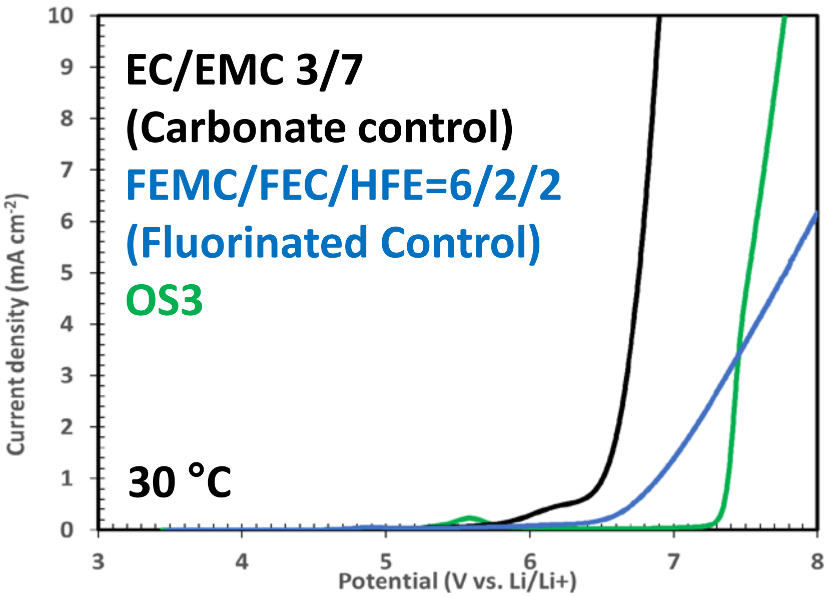


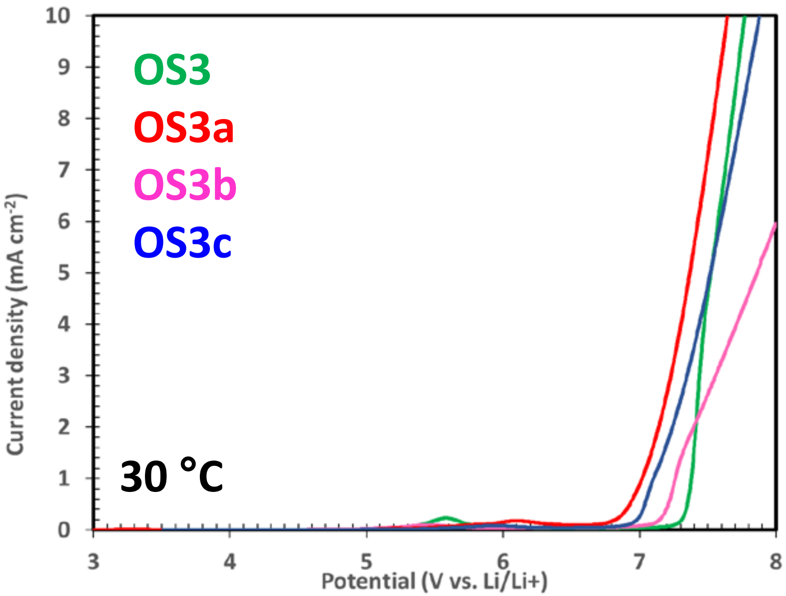
FEMC



HFE

LSV (Linear Scan Voltammetry) of OS3 Family Solvents and Controls at Pt Electrode (OCV to 8 V).
All electrolytes with 1M $LiPF_6$ salt.





- <u>Voltage stability</u>: OS3 > Fluorinated Control > Carbonate Control
- All OS3 family solvents show higher breakdown voltages than controls.

Technical Accomplishment: Floating Tests of OS3 and Controls

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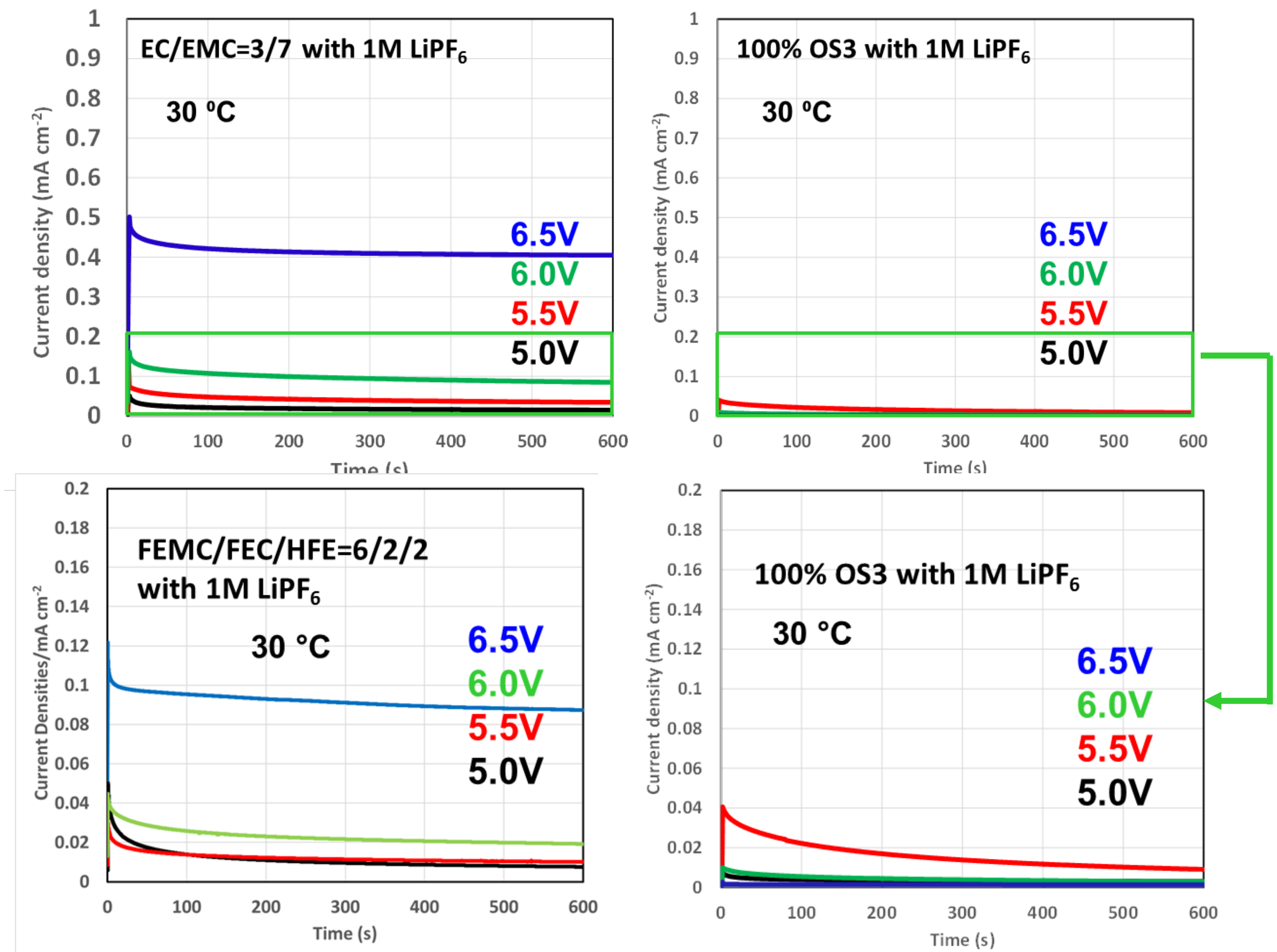
Floating Test of OS3 Family Solvents and Controls at Pt Electrode (4.5-6.5 V, 10 min at each voltage. Test Condition: 30°C)



Carbonate control displays much higher parasitic current values than OS3 at higher voltages.

Fluorinated electrolyte displays higher floating current values than OS3 at higher voltages.

Technical Accomplishment: Electrochemical Behavior of OS3 Family Solvents

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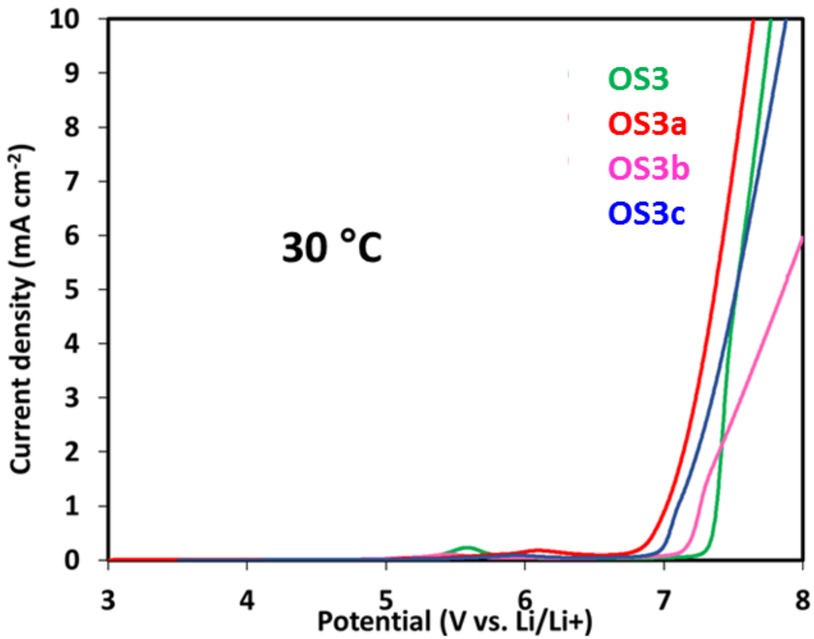
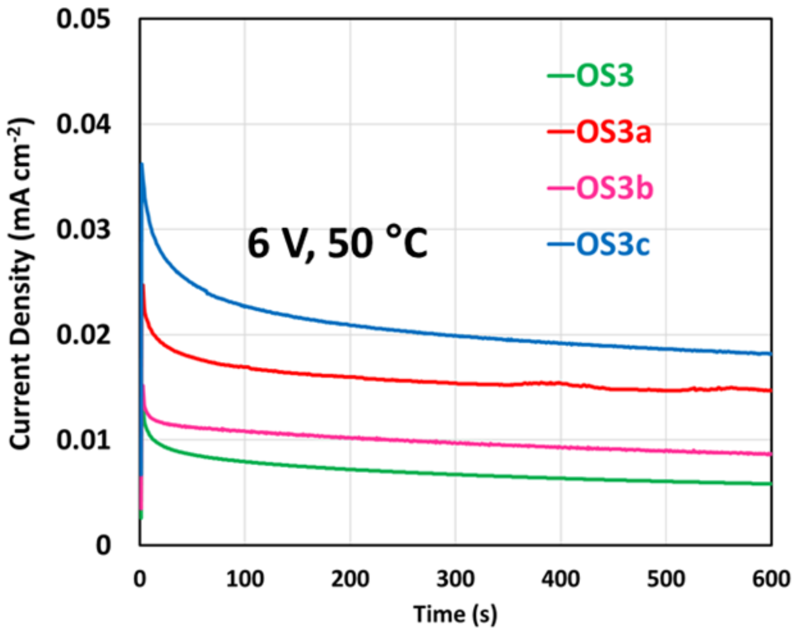
LSV and Floating tests of OS3 Family Solvents at Pt Electrode (all with 1M $LiPF_6$)





- Four OS3 family solvents satisfied the Go/No-Go Metric #1 (breakdown potentials > 6V at 30°C with $LiPF_6$) and are good candidates for HV systems.
- The floating currents of these OS3 family electrolytes satisfied Go/No-Go Metric #2 (50°C parasitic current <0.02 mAh/cm^2 at 6V).

Technical Accomplishment: Floating Tests in Fluorinated Electrolytes (LNMO/Li Half Cell)

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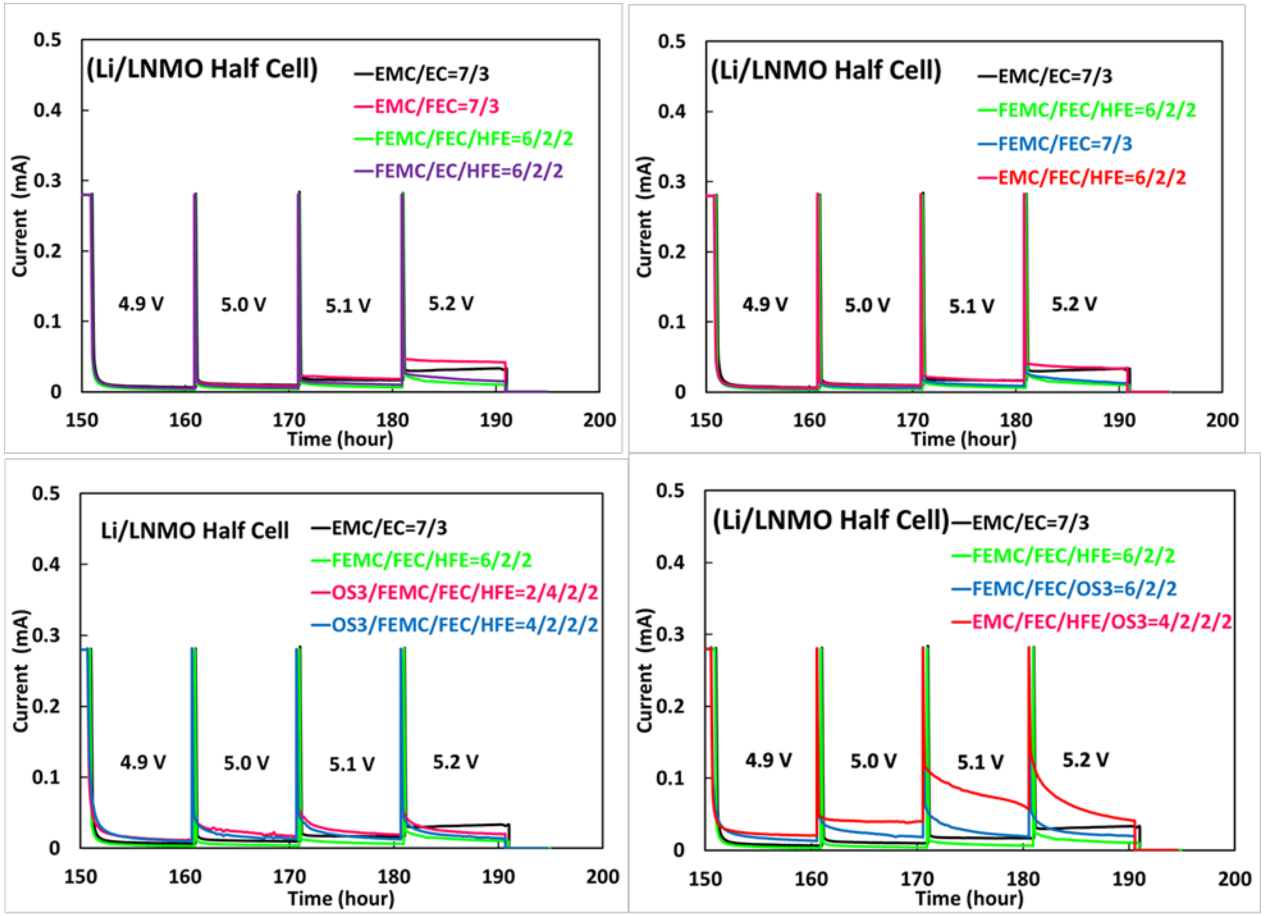
Cathode half cells (LNMO/Li) are cycled at C/20 for 2 cycles (3.5-4.9 V) and C/2 for another 10 cycles (3.5-4.9 V), then charged at C/20 again to 4.9V, hold for 10h at each voltage until 5.2V.



- Similar current observed when replacing FEC with EC in fluorinated electrolytes. EC can be applied in the fluorinated system to enhance overall conductivity and cell performance.
- FEMC/FEC showed a similar current to FEMC/FEC/HFE.
- Addition of OS3 to the fluorinated control lowers parasitic currents above 5.1 V.
- FEMC is more compatible with OS3 compared to EMC.

Technical Accomplishment: Cycling Tests in OS containing Electrolytes (LNMO/graphite Full Cell)

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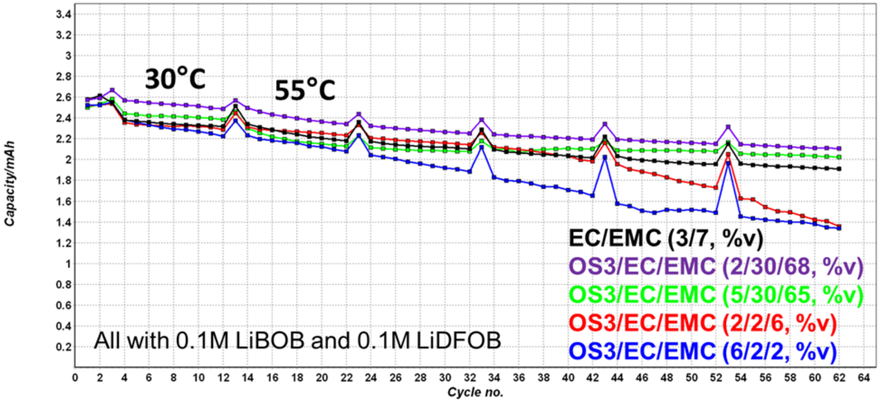
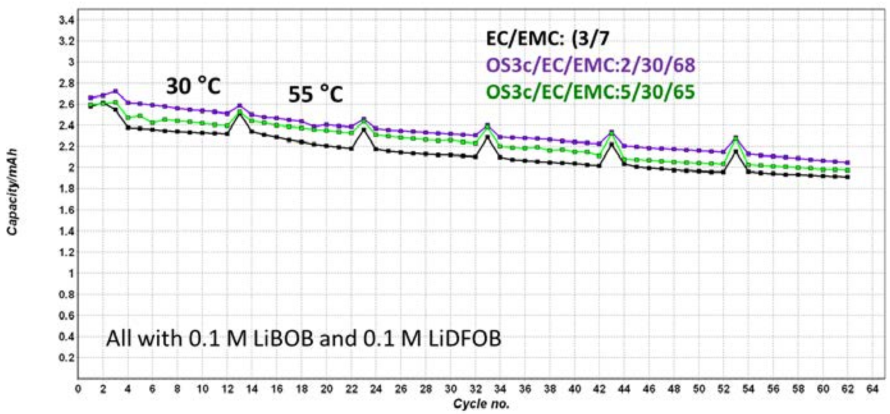
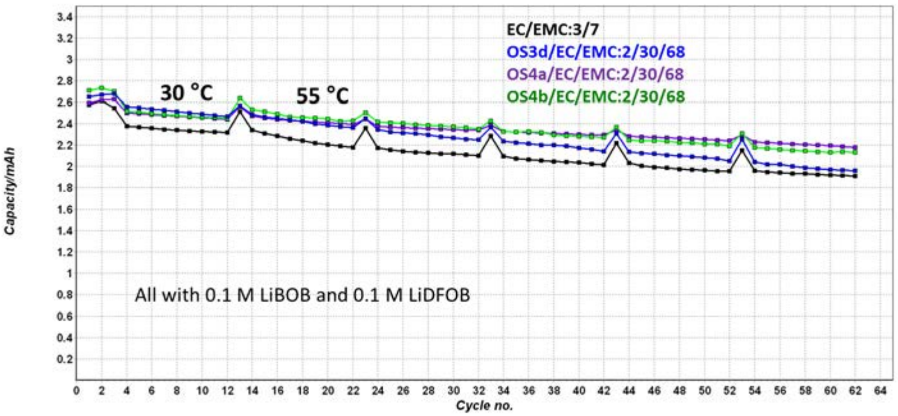
Cycled at C/20 for 2 cycles and C/2 for 10 cycles at 30°C, then 50 cycles at 55°C with C/2. Voltage Window: 3.5-4.9 V.



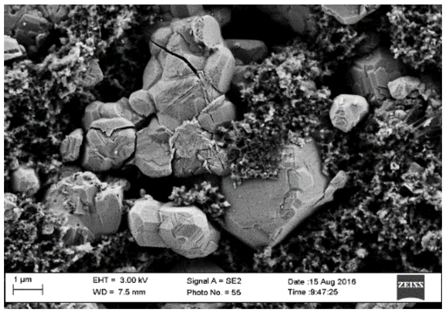
- Low OS3 electrolytes (2% or 5%) show greater capacity retention compared to the control after 50 cycles at 55°C. Higher OS3 concentrations (20% or 60%) result in greater capacity degradation.
- OS3c (2% or 5%) performs similarly to OS3..
- Both low OS3 and OS3c concentration electrolytes were selected for 1st pouch cell build.
- OS3d, OS4a and OS4b show improved capacity retention compared to the carbonate control and will be optimized for 2nd pouch cell build.



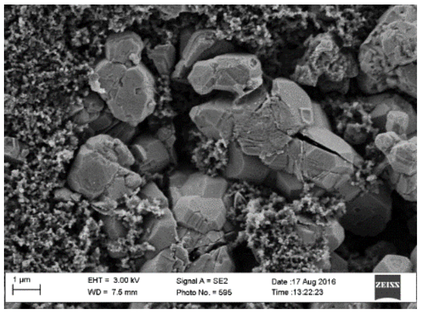


Technical Accomplishment: Surface Analysis (LNMO/graphite full cell)

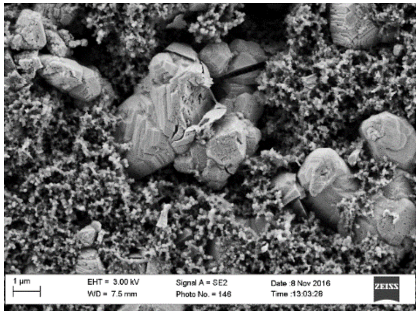
Control (EC/EMC=3/7)



2% OS3 (in Control)



2% OS3c (in Control)

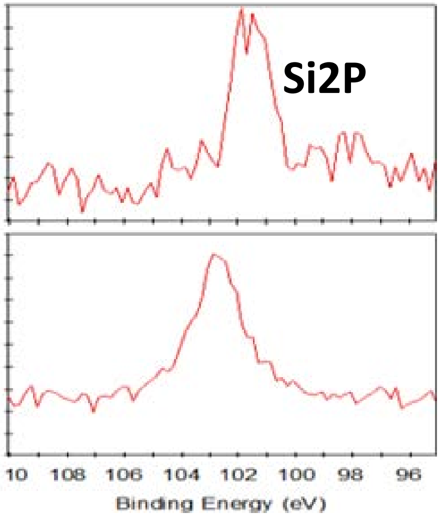


SEM analysis shows the surface morphology of the cathodes is similar regardless of the formulation after 50 cycles at 55°C.

Cathode surface

2% OS3 (in Control)

2% OS3c (in Control)



- XPS surface analysis showed silicon present on cathode samples after 50 cycles at 55°C with 2% OS3 and OS3c electrolytes, indicating that OS solvents are involved in cathode film formation.
- Similar results were obtained for anode samples after 50 cycles at 55°C, which means OS solvents also participate in anode SEI formation.

Technical Accomplishment: DSC Tests (LNMO/graphite full cell)

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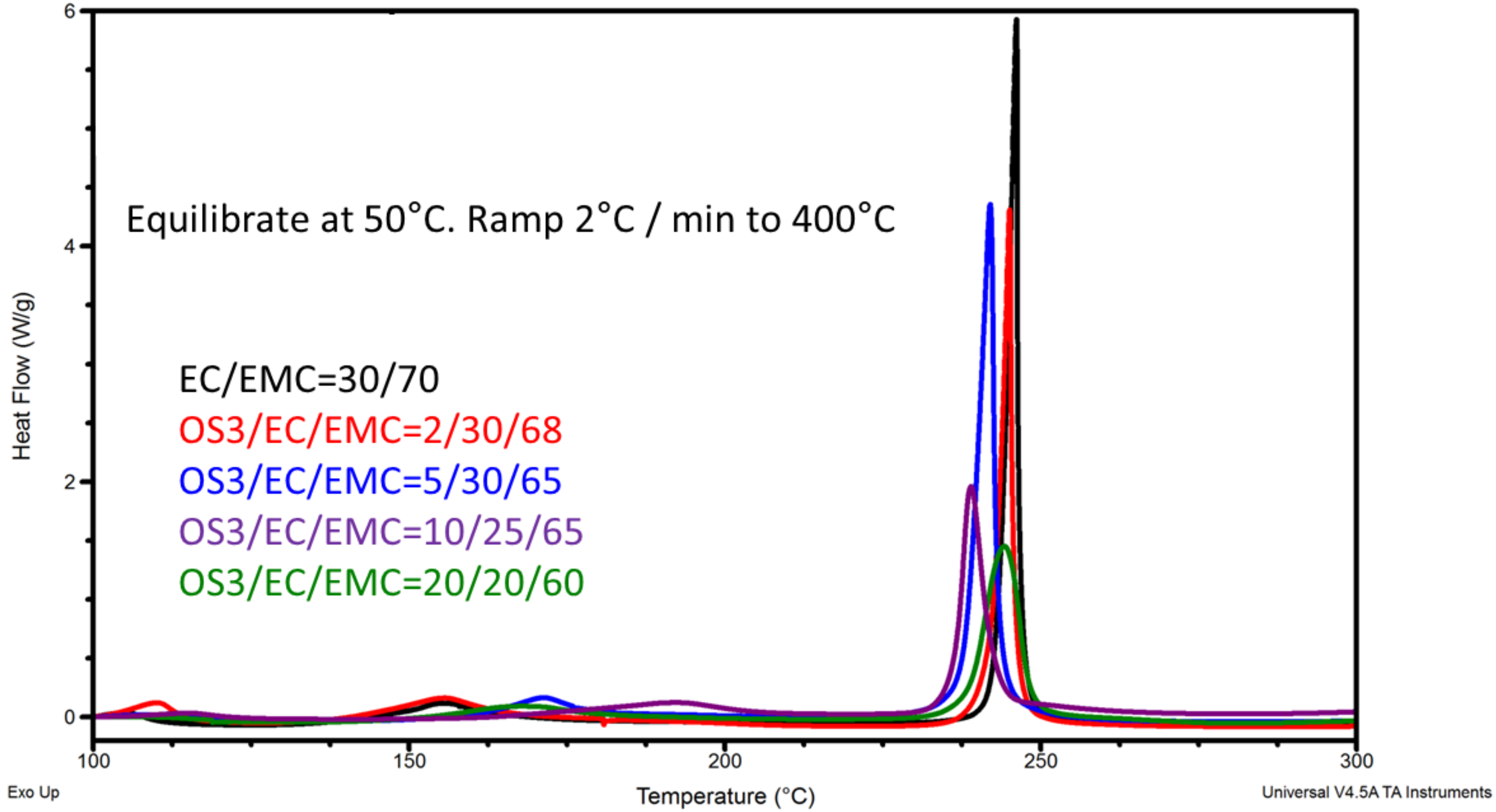
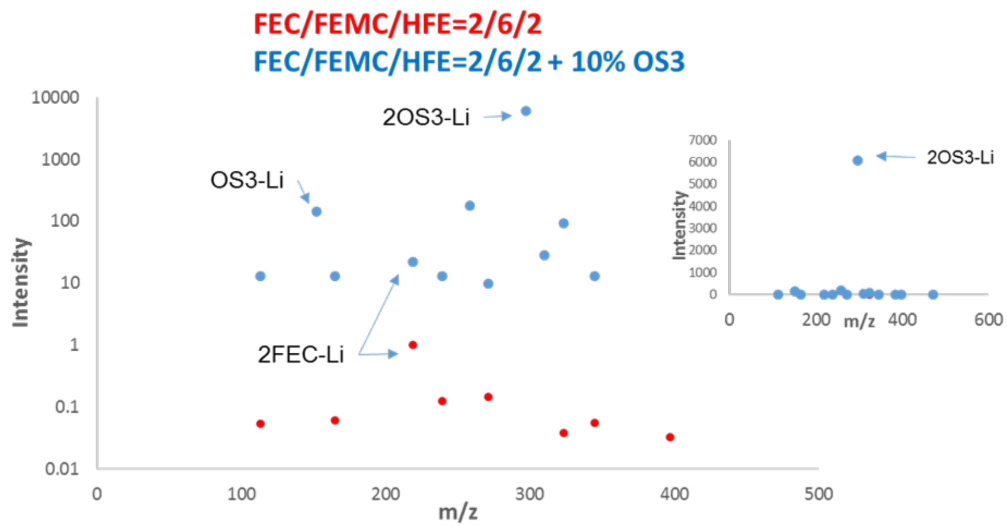
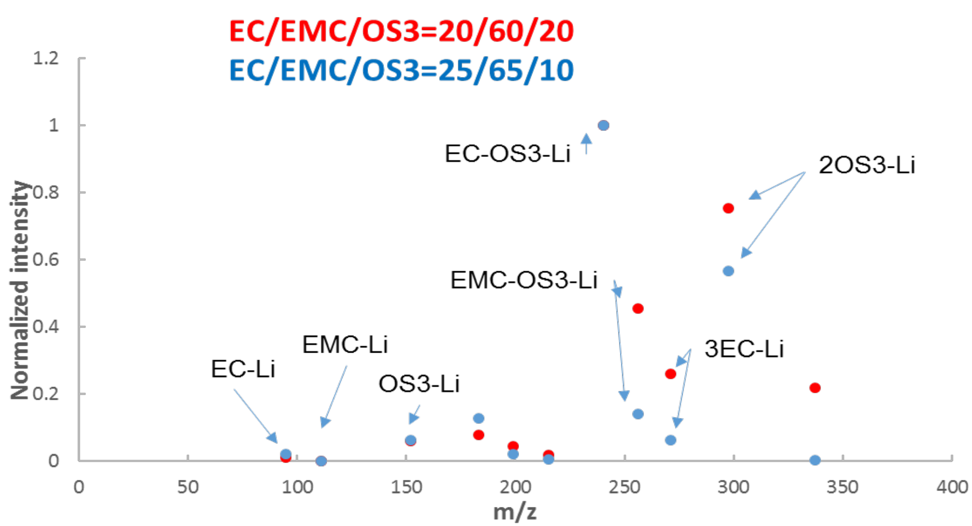
- Differential scanning calorimetry of de-lithiated cathode found increasing OS3 concentration decreases the magnitude of primary exotherm.
- Onset temperature is equivalent.



Technical Accomplishment: ESI-MS (Solvation)

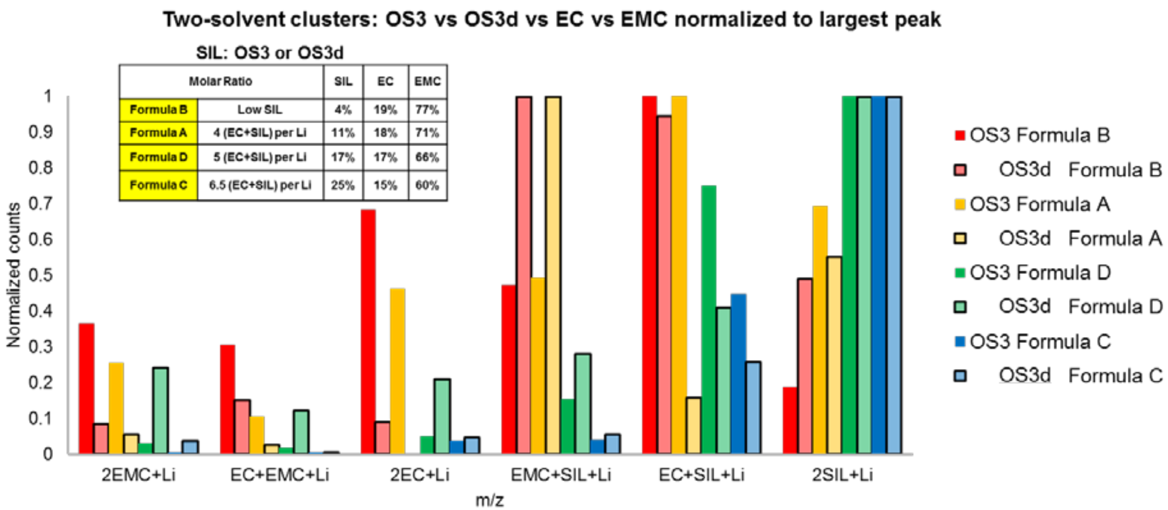


- Without OS3, FEC is the strongest solvator in the FEC/FEMC/HFE electrolyte.
- When added, OS3 dominates all fluorinated solvents for Li^+ solvation.

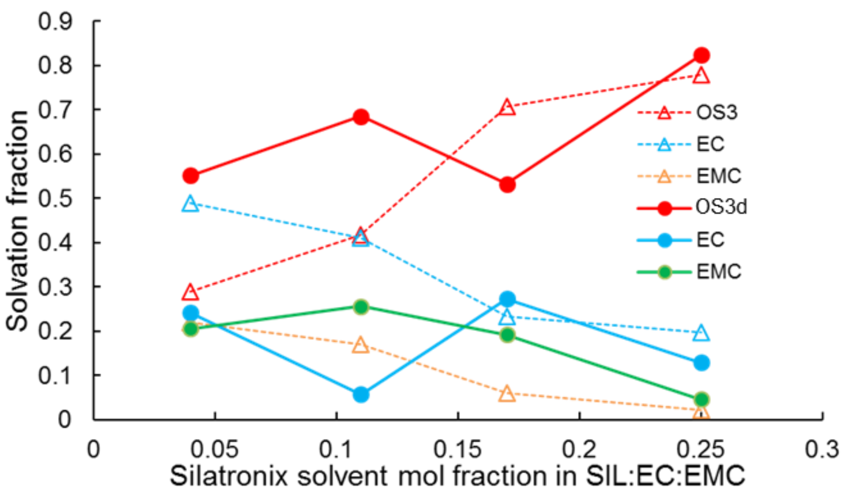


- OS3 is a strong competitor for EC in Li^+ solvation and OS3-EC clusters are observed.
- $2OS3\text{-}Li^+$ cluster was the strongest peak in both cases

Technical Accomplishment: ESI-MS (Solvation)



- Both OS3 and OS3d consistently coordinate Li^+ more strongly than EC or EMC.
- Clusters of Li^+ with two solvents were the best represented in ESI-MS data.
- OS3d had a larger population of OS3d+EMC clusters. In contrast, OS3+EC was the dominant 2-solvent cluster.



<u>OS3 vs. OS3d</u>

- OS3d appears to displace carbonate solvents more than OS3.
- By comparison, OS3d is a stronger Li^+ solvator than OS3 in carbonate containing electrolytes, even at 4 mol% OS3d.

Technical Accomplishment: NMR Solvation (What can we learn from binary systems?)

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NMR chemical shift (δ_A) changes with chemical environment (Li^+ coordination).
Normalized NMR chemical shift (S_A) calculated to compare strength of coordination.

$$S_A = [\delta_A(L, M) - \delta_A(M)]/[\delta_A(L) - \delta_A]$$

$\delta_A(L,M)$ = shift of solvent A in mixture with salt
$\delta_A(M)$ = shift of solvent A in mixture without salt
$\delta_A(L)$ = shift of solvent A with salt
δ_A = shift of solvent A without salt

Example Data: EC/EMC/OS3 Electrolytes

Normalized NMR shift

	Ternary Mixtures	Solvent per Li			EC		EMC	OS3	
		OS3	EC	EMC	CO3	CH2	CO3	CN	15N CN
B	Low OS3	0.5	2.5	10	2.3	2.6	0.9	0.7	0.6
A	4 (EC + OS3)	1.5	2.5	10	2.3	2.7	1.1	0.7	0.6
D	Equal OS3	2.5	2.5	10	2.3	2.7	1.3	0.7	0.6
C	Excess OS3	4	2.5	9.7	2.4	2.8	1.5	0.7	0.7

- EC shows same coordination strength in all ternary mixtures – expected due to constant EC/Li^+ ratio.
- OS3 coordination does not vary significantly with OS3 concentration.
- EMC coordination increases with increasing OS3 concentration.

Technical Accomplishment: NMR Solvation (What can we learn from binary systems?)

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NMR chemical shift (δ_A) changes with chemical environment (Li^+ coordination).
Normalized NMR chemical shift (S_A) calculated to compare strength of coordination.

OS3/EC/FEMC
Normalized NMR shift

7/2/1 (vol)	FEMC (5.8M)	EC (3M)	OS3 (0.64M)	
	CO_3	CO_3	CN	15N CN
S	0.7	2.9	0.8	0.9
6/2/2 (vol)	FEMC (5.0M)	EC (3M)	OS3 (1.3M)	
	CO_3	CO_3	CN	15N CN
S	0.7	2.8	0.7	0.8
4/2/4 (vol)	FEMC (3.3M)	EC (3M)	OS3 (2.6M)	
	CO_3	CO_3	CN	15N CN
S	0.5	2.0	0.4	0.5

- At a constant EC concentration (3M), increasing OS3 content decreases EC coordination.

OS3/FEC/FEMC
Normalized NMR shift

7/2/1 (vol)	FEMC (5.8M)	FEC (2.7M)	OS3 (0.64M)	
	CO_3	CO_3	CN	15N CN
S	1.0	1.8	1.0	1.2
6/2/2 (vol)	FEMC (5.0M)	FEC (2.7M)	OS3 (1.3M)	
	CO_3	CO_3	CN	15N CN
S	1.0	1.7	0.9	1.2
4/2/4 (vol)	FEMC (3.3M)	FEC (2.7M)	OS3 (2.6M)	
	CO_3	CO_3	CN	15N CN
S	1.0	1.5	0.8	1.1

- Solvation in fluorinated blends similar as a function of concentration.
- FEMC shows no variation with composition.
- FEC shows reduced Li^+ coordination strength as the OS3 content increases.

Response to Reviewers Comments

Comment #1: The reviewer suggested to select and optimize the solvents/additives in full cells.
Response #1: We have focused our evaluation of OS formulations in LNMO/graphite full cells.

Comment #2: The reviewer commented that more attention should be paid to low-temperature performance.
Response #2: We are working to optimize HV electrolytes and are using performance at high temperature as a metric to better provide differentiation in HV performance. We understand the importance of low-temperature performance for specific applications, however it is beyond the scope of this development program.

Comment #3: The reviewer noted that there was no explanation of OS structure or design strategy, and asked about the purity of OS materials.
Response #3: We design and synthesize new materials based upon rational molecular design, investigation of different functional groups and theoretical modeling, to achieve the superior oxidative stability required for HV applications. The purity of OS materials have been checked by NMR and GC, which are above 99.9% for battery testing.

Collaboration and Coordination

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Collaborators:

- **U.S. Army Research Laboratory (Kang Xu, Project team member)**
- **Argonne National Laboratory (Bryant Polzin, Project team member)**

Interactions:

- **University of Wisconsin Madison (Facilities Use in Chemistry Department and UW Advanced Materials Consortium)**
- **APS Center at Argonne National Laboratory (XANES Experiment)**

Remaining Challenges and Barriers

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- The first round of pouch cell tests using EC/EMC control and 3 OS formulations have been tested at ANL in this quarter. However, all pouch cells are showing a large amount of gassing and we can not complete the evaluation of cycling performance in pouch cells.

- To offset this phenomenon, we are investigating the role of both OS and carbonate solvents in gas generation and optimizing the composition of the final formulations to reduce gassing and enable capacity retention testing.

- Additional optimization of the additive package could increase compatibility with OS solvents and improve capacity retention.

Proposed Future Work

- Silatronix and ARL will continue to optimize HV electrolyte formulations
  - Electrolyte formulations will be developed with select OS solvents and additives for the 5V LNMO full cell system to address gas generation.
  - Additional surface analysis and XANES experiments will be conducted to investigate the fundamental mechanisms underlying OS performance in the 5V LNMO cell to provide direction for electrolyte optimization.
- Top performing HV electrolyte formulations will be tested in 2nd round 5V LNMO/graphite pouch cells (13 layers, 200-300 mAh) at ANL.
- Based on past experience at ANL for LNMO pouch cells, reduced gassing has been achieved if the upper voltage cut off is reduced to 4.7 V.
  - ANL will conduct the same tests (Formation, Rate Study, HPPC and Cycle Life) with the new voltage window (3.5-4.7 V) in a second pouch cell build with additional optimized OS formulations.
  - If less gassing is observed after formation and rate tests, a set of pouch cells may be tested with an upper voltage cut off of 4.8V.

Any proposed future work is subject to change based on funding levels.

Summary of Technical Accomplishment

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- OS3 solvent family shows excellent oxidative stability with a wider electrochemical stability window and lower floating currents above 4.5V compared to controls.
  - 12 OS solvents have been synthesized and evaluated.
  - 4 OS solvents met the Go/No Go technical metric.
- FEMC was identified as a key solvent for high voltage stability compared to EMC by LNMO/Li half cell floating tests.
- Electrolytes with less than 5% OS show comparable or improved HT cycling stability compared to the EC/EMC (3/7, %v) control. Low OS content electrolytes were chosen for the 1st pouch build at Argonne National Laboratory.
- Additive selection is an important factor in full cell cycling, especially for OS electrolytes. Army Research Laboratory synthesized and screened ten additives for performance improvement. Five additives were shipped to Silatronix for evaluation.
- Surface analysis found evidence that OS solvents participate in cathode and anode surface layer formation.
- DSC tests performed on de-lithiated LNMO cathodes showed that OS3 addition reduces the magnitude of the primary exotherm without a significant change in onset temperature.
- Solvation studies identified OS3 solvents as high-affinity Li^+ solvents based upon ESI-MS and NMR spectroscopy measurements. Therefore, they could impact SEI formation.

Technical Back-Up Slides

Electrochemical behavior of OS3d

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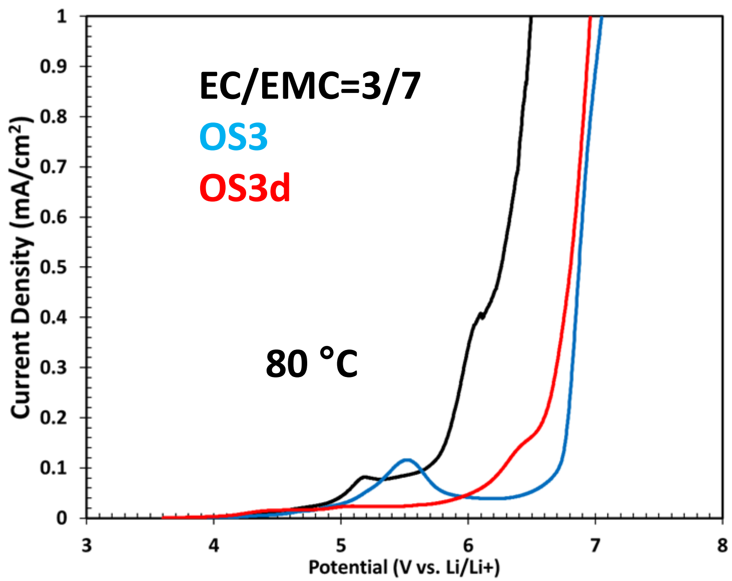
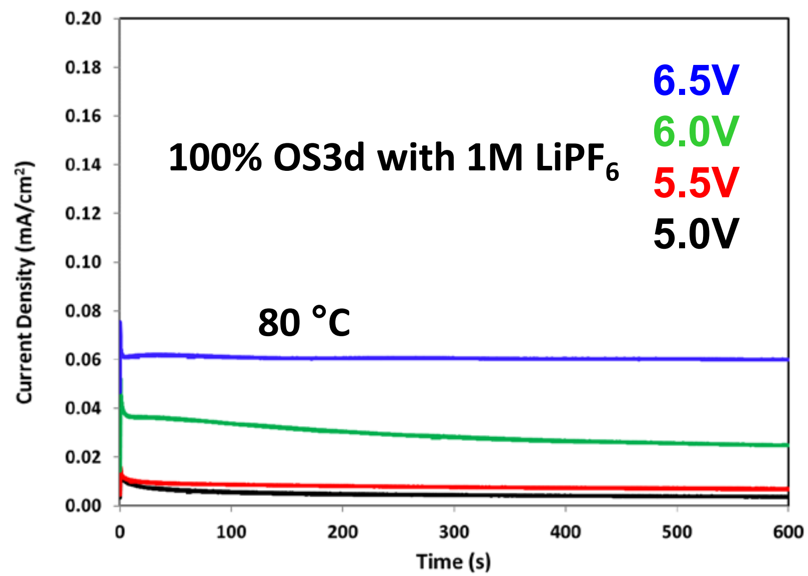
LSV and Floating tests of OS3d and OS3 at Pt Electrode, all with 1M $LiPF_6$ salt. (Test Condition: 80 °C)





OS3d is solid at 30 °C, LSV was tested at 80 °C and show better voltage stability between 5 and 6 V than OS3 and carbonate control.

Great oxidative stability below 6 V during floating tests even at 80 °C.

Electrochemical behavior of OS4a and OS4b

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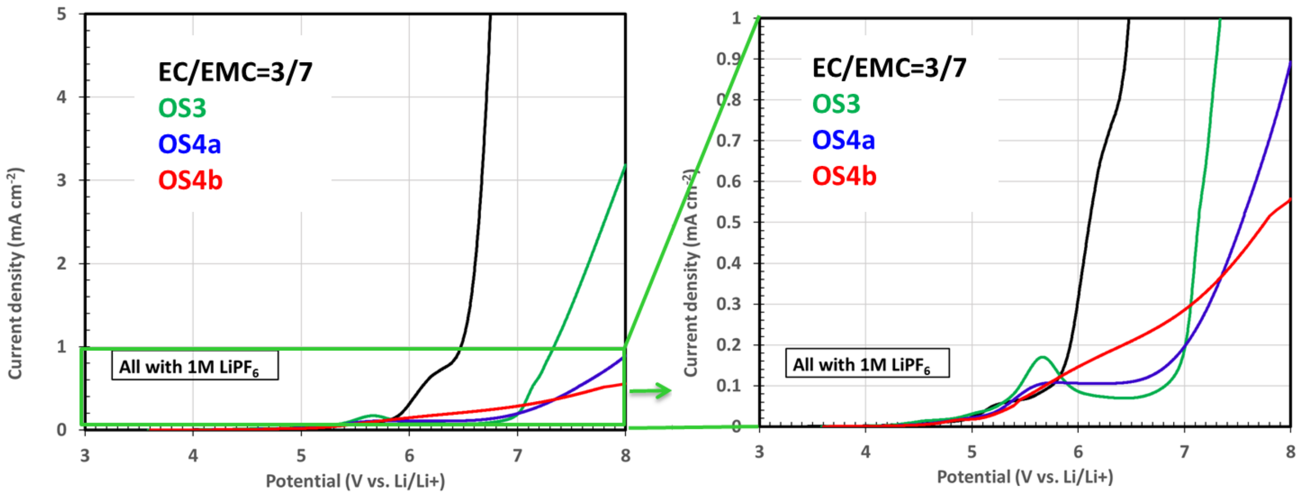
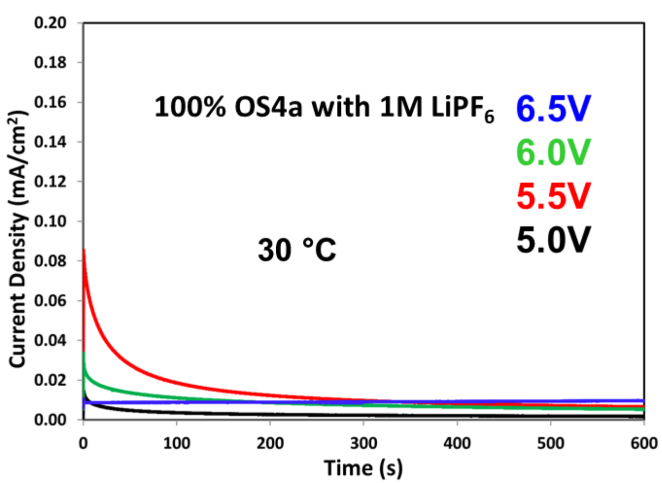
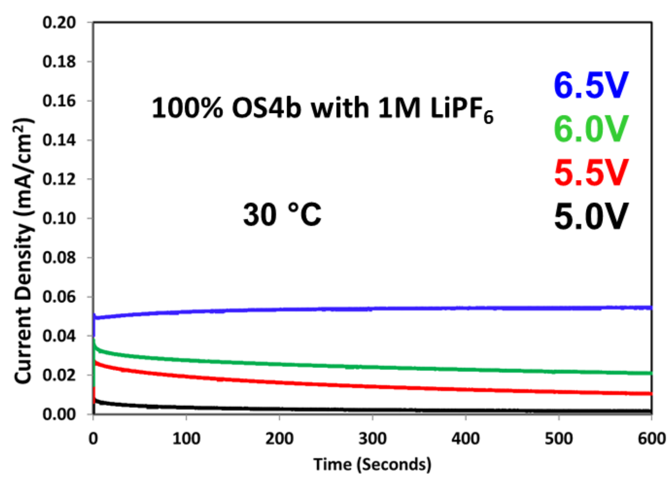
LSV and Floating tests of OS4a and OS4b at Pt Electrode, all with 1M $LiPF_6$ salt. (Test Condition: 30 °C)



Both OS4a and OS4b solvents demonstrate a higher breakdown voltage than carbonate control.





OS4a shows the highest current response at 5.5V similar to OS3 family solvents and OS4b shows increasing floating current with each voltage step similar to carbonate control.